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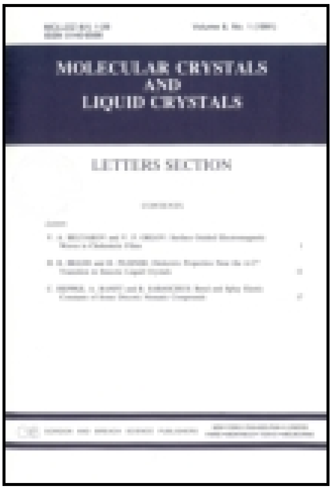

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Solution-Processable Low Voltage Organic Transistors of Thieno[3,2-*b*]thiophene-Based Conducting Polymer

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*A low-operating voltage and high performance polymeric field effect transistors using octadecylphosphonic acid-treated high-*k *AlOx and HfO_2 hybrid dielectrics were demonstrated. High-*k *metal oxide hybrid dielectrics were prepared by oxygen plasma treatment of deposited Al film for AlOx and by spin coating of solution-processable HfO_2 sol-gel solution for HfO_2 in combination with phosphoric acid-based self-assembled monolayer (SAM), resulting in high capacitance (10 nF/cm^2 for SiO_2, 600 nF/cm^2 for AlOx and 580 nF/cm^2 for HfO_2). With phosphoric acid-based SAM on high-*k *metal oxide and thermal annealing of thieno[3,2-*b*]thiophene-based conducting polymer, the device performance was significantly enhanced. The highest mobility of the transistors using ODPA-treated AlOx as a gate dielectric is 2.3×10^{-2} cm^2 V^{-1} s^{-1} in the saturation region with the source-drain of −2 V. In ODPA-treated HfO_2 hybrid dielectric, the saturated mobility is 1.1×10^{-2} cm^2 V^{-1} s^{-1} and the threshold voltage was measured to be −0.31 V, which is at least one order lower than SiO_2 hybrid dielectric (−3 V).*

Keywords Organic transistors; low-operating voltage; thieno[3; 2-*b*]thiophene-based polymer; dielectrics

Introduction

In recent years the pursuit of ubiquitous low cost flexible electronics has been magnified with tremendous researches on organic thin film transistors (OTFTs). Since the TFT is the most fundamental element for a large number of electronic devices, solving materials related barriers that address the interplay between the processing, properties, and performance of OTFTs will expedite the integration of OTFTs into promising applications such as flexible displays, radiofrequency identification tags (RFID), and sensors. A significant challenge

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lies in developing compatible all solution processed organic semiconductor (OSC)/gate dielectrics systems that allow low-voltage OTFT operation with high performance [1].

Low-voltage devices are achieved by increasing the capacitance density of the gate dielectric (C_i). In these devices, the dielectric materials play an important role in reducing the operating voltage. Conventionally gate dielectrics in combination with densely packed self-assembled monolayer have been proven to be good candidates in low-voltage OTFTs [2–4]. Controlling interface between the semiconducting layer and the gate dielectric can be improved device performances [5, 6].

Recently, Jen's group has developed solution processed organic monolayer/high-*k* metal oxide hybrid dielectrics for low-voltage OTFTs utilizing plasma-treated AlOx and sol-gel hafnium oxide with phosphonic acid based SAMs [7, 8]. Typically, alkyl based SAMs are used for improving the device performance in polythiophene based OTFTs due to their compatible interactions with the side alkyl chains of the polymer promoting a two-dimensional lamellar structure at the OSC/dielectric interface [9]. In literatures, liquid-crystalline conjugated polymers have been investigated as a semiconductor. Although poly(3-hexylthiophene) (P3HT), [10] poly(3,3-didodecylquarterthiophene) (PQT-12), [11, 12] and poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophene) (PBTTT) [13] have distinguished mobility characteristics due to the strong cofail π-π interaction and structural uniformity, their transistors show poor oxidative stability resulted from their high highest occupied molecular orbital (HOMO) level (4.9~5.1 eV). Here we has introduced high capacitance dielectric system to solution processed OSCs by demonstrating OTFTs operating under 1.5 V. To increase device performance with relatively low operating voltage we have designed and synthesized 3-octyl thieno[3,2-*b*]thiophene based polythiophene derivative, named as Poly(TT-BT).

Experimental

Materials and Instrumentation

3-Bromothiophene, 1,5-cyclooctadiene, *N*-bromosuccinimide (NBS), 2,2′-dipyridyl, octadecyltrichlorosilane (OTS), bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), octadecylphosphonic acid (ODPA), dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$), and hafnium(IV) chloride ($HfCl_4$) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Toluene and tetrahydrofuran (THF) were distilled over calcium hydride and sodium benzophenone ketyl, respectively, under nitrogen prior to use. 3-Octylthieno[3,2-*b*]thiophene [14] and 5,5′-bis(tributylstannyl)-2,2′-bithiophene [15] were prepared according to the methods described in the literature.

^1H and ^{13}C NMR spectra were measured using a Bruker 300 instrument spectrometer. High-resolution mass spectrometry (HRMS) was performed by the UW Bio Mass Spectrometry Lab. UV-vis absorption spectra were measured using a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. Thermal transitions were measured on TA Instruments differential scanning calorimeter (DSC) 2010 and thermogravimetric analysis (TGA) 2950 under nitrogen atmosphere at a heating rate of 10°C/min. The molecular weight and polydispersity were analyzed by a Waters 1515 gel permeation chromatograph (GPC) with a refractive index detector at room temperature (THF as the eluent). Cyclic voltammetric measurement was performed on a BAS CV-50W voltammetric system with a three electrode cell in a solution of 0.1 M $Bu_4N{\cdot}PF_6$ in acetonitrile and CV curves were calibrated using ferrocence as the standard. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated by using the equations $E_{\mathrm{HOMO}} = -(\mathrm{E}_{\mathrm{ox}} + 4.8)$ eV and $E_{\mathrm{LUMO}} = E_g + E_{\mathrm{HOMO}}$, respectively. Contact angles were measured using a contact angle meter (CAM 100, KSV Instrument).

Synthesis

Compound 2: To a solution of 1 (1.01 g, 4.0 mmol) in acetic acid (15mL) *N*-bromosuccinimide (0.71 g, 4.0 mmol) was added at room temperature. The mixture was stirred at 60°C for 3 h. After being cooled down to rt, the solution was extracted with ethyl acetate and water. After the removal of organic solvent, the residue was purified by column chromatography on silica using hexane as eluent to obtain 2-bromo-3-octylthieno[3,2-*b*]thiophene (1.0 g, 75%) as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, 3H), 1.35 (m, 10H), 1.75 (m, 2H), 2.80 (t, 2H), 7.20 (d, 1H), 7.42 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.13, 22.68, 28.66, 29.27, 29.38, 29.41, 29.95, 31.88, 110.1, 119.4, 125.7, 134.1, 136.8, 138.3.

Compound 3: To a solution of 2 (1.10 g, 1.48 mmol) in THF (20 mL) 5,5′-bis(tributylstannyl)-2,2′-bithiophene (1.08 g, 3.25 mmol) and $PdCl_2(PPh_3)_2$ (52 mg, 0.07 mmol) were added to a stirring mixture. After the solution was stirred for 12 h at 80°C, dichloromethane (200 mL) was added to the solution. The organic layer was washed with brine (30 mL) and dried over anhydrous magnesium sulphate ($MgSO_4$). The residue was purified by column chromatography on silica using hexane as eluent to obtain 5,5′-bis(3-octylthieno[3,2-*b*]thiophen-2-yl)-2,2′-bithiophene (0.67 g, 80%) as yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 6H), 1.29-1.48 (m, 20H), 1.82 (m, 4H), 2.97 (t, 4H), 7.11 (d, 2H), 7.19 (d, 2H), 7.26 (d, 2H), 7.40 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 22.67, 28.95, 29.04, 29.22, 29.32, 29.65, 31.88, 119.67, 123.98, 126.68, 126.79, 131.85, 131.86, 135.64, 136.39, 137.11, 141.59; HRMS (ESI) (M+, $C_{36}H_{42}S_6$): calcd: 666.1611; found: 666.1607.

Compound 4: 3 (0.2 g, 0.3 mmol) was dissolved in 20 mL of AcOH:$CHCl_3$ (1:1). *N*-Bromosuccinimide (0.11 g, 0.63 mmol) was added in one portion. The mixture was stirred for 1 h. The precipitated solid was filtered and washed with MeOH. The resulting yellowish solid was directly purified by column chromatography on silica using hexane as eluent to obtain 5,5′-bis(5-bromo-3-octylthieno[3,2-*b*]thiophen-2-yl)-2,2′-bithiophene (0.22 g, 89%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, 6H), 1.29-1.48 (m, 20H), 1.76 (m, 4H), 2.90 (t, 4H), 7.09 (d, 2H), 7.18 (d, 2H), 7.24 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 22.67, 28.90, 28.92, 29.19, 29.30, 29.58, 31.86, 113.10, 122.37, 124.15, 127.04, 131.61, 131.61, 135.10, 135.34, 137.27, 141.63; HRMS (ESI) (M+, $C_{36}H_{40}Br_2S_6$): calcd: 821.9821; found: 821.9817.

Synthesis of poly(5,5′-bis(3-octylthieno[3,2,-*b*]thiophen-2-yl)-2,2′-bithiophene) (Poly (TT-BT)): $Ni(COD)_2$ (88 mg, 0.32 mmol) was dissolved in 20 mL of anhydrous toluene at room temperature under a nitrogen atmosphere. After $Ni(COD)_2$ was dissolved, 2,2′-dipyridil (52 mg, 0.33 mmol) and catalytic amount of 1,5-cyclooctadiene were added and stirred for 30 min. Compound 4 (220 mg, 0.27 mmol) was added and refluxed for 48 hrs. After 48 h, the reaction mixture poured into methanol. The crude polymeric product was filtered off and washed with MeOH. The precipitate was extracted (*via* Soxhlet) with hexane, acetone, and methanol for 24 h each. Finally the polymer was dissolved in hot chlorobenzene and precipitated in methanol. The polymer was dried in a vacuum oven at 50°C for 1 day, yielding 150 mg (40%) dark metallic solid. By using gel permeation chromatography, the molecular weight (Mn) and polydispersity index of Poly (TT-BT) was determined to be 1.82×10^4 g mol^{-1} and 1.7 relative to polystyrene standard, respectively.

Device Fabrication and Characterization

Top contact OFETs were fabricated on heavily n-doped silicon substrates (Montco Silicon Technologies, Inc.) with a 300 nm thick thermally grown SiO_2 dielectric, or given SAM/MO hybrid dielectric. Before organic semiconductor deposition, the 300 nm SiO_2 dielectric substrates were treated with octyltrichlorosilane (OTS) by vapor phase deposition in a vacuum oven (200 mTorr, 80°C, 5 h). AlOx and HfO_2 based dielectrics were prepared by modified literature method [16]. The Poly(TT-BT) semiconductor films were spin-coated at in air from a 1 wt% 1,2-dichlorobenzene solution heated at 60°C followed by a 160°C bake on a hotplate for 10 min in an argon environment. Interdigitated source and drain electrodes ($W = 9000\ \mu m$, $L = 90\ \mu m$, $W/L = 100$) were defined by evaporating a 50 nm thick gold film through a shadow mask from a resistively heated Mo boat at 10^{-6} Torr. All OFETs and J-V characterization were performed under ambient conditions and completed within six hours of first exposure using an Agilent 4155B semiconductor parameter analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of $(-I_{ds})^{1/2}$ versus V_{gs}. The threshold voltage (V_t) was estimated as the x intercept of the linear section of the plot of $(-I_{ds})^{1/2}$ versus V_{gs}. The subthreshold swing was calculated by taking the inverse of the slope of −Ids versus V_{gs} in the region of exponential current increase. An Agilent 4192 Impedance Meter was used for capacitance characterization of the different dielectrics for frequencies from 100 Hz to 100 kHz. 1 mm in diameter circles of thermally evaporated gold were used as the top electrode and the heavily doped silicon was used as the bottom electrode. Capacitance values were taken at 10 kHz. Digital Instruments Multimode Nanoscope IIIa scanning probe microscope was used in AFM taping mode. Tips were etched silicon tips with a typical resonant frequency of 300–350 kHz.

Results and Discussion

The synthesis of the conjugated polymer (Poly(TT-BT)) is summarized in Fig. 1. The details for the synthesis and characterization of compounds are presented as the following: The 5,5′-Bis(3-octylthieno[3,2-*b*]thiophen-2-yl)-2,2′-bithiophene (3) was prepared by Stille coupling reaction between the 5,5′-(tributylstannyl)-2,2′-bithiophene and 2-bromo-3-octylthieno-[3,2,-*b*]thiophene (2), followed by bromination with *N*-bromosuccinimide to give compound (4). The chemical structure of monomers was identified by ^1H, ^{13}C-NMR

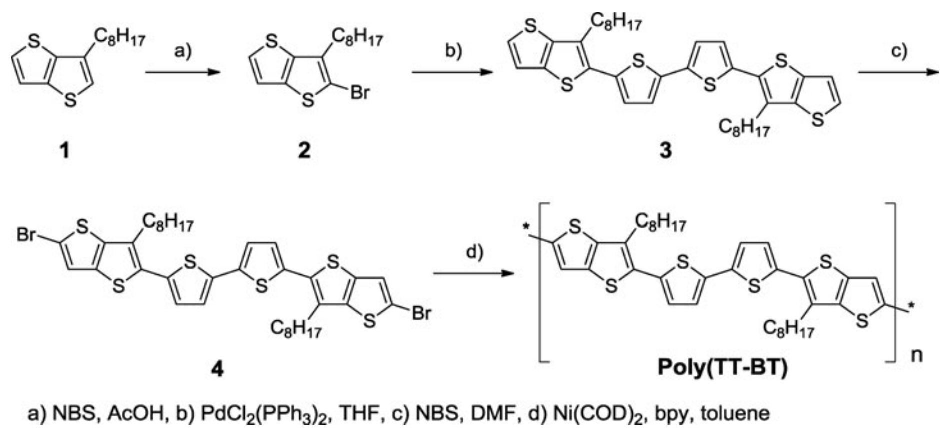

Figure 1. Synthesis of octyl-substituted thieno[3,2,-*b*]thiophene-based polymer (Poly(TT-BT)).

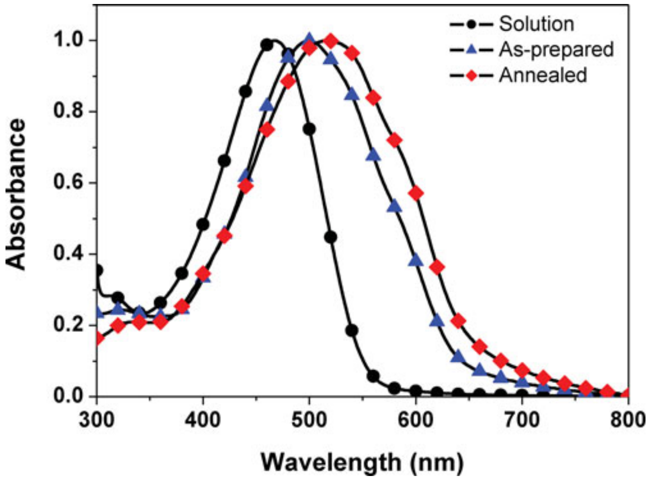

Figure 2. Normalized UV-vis absorption spectra of Poly(TT-BT) solution (1,2-dichlorobenzene) and film before and after annealing (at 160°C for 10 min).

and mass. In NMR spectrum, after Stille coupling reaction between compound 3 and tin compound, the tributyl protons of bithiophene moiety ($-\mathrm{Si}Bu_3$, 27H) were clearly disappeared and the observed heteroaromatic protons were shown as 4 doublet peaks in the range of 7.11~7.4 ppm. After bromination, C-4 proton in 3-octyltheino[3,2-*b*]thiophene unit was simplified from a doublet to a singlet (7.24 ppm) and no C-5 proton was observed, indicating replacement of C-5 hydrogen atom with a bromine atom. The polymerization was carried out in the presence of Ni(COD)$_2$ (COD: 1,5-cyclooctadiene), 2,2-dipyridil and a catalytic amount of 1,5-cyclooctadiene in reflux toluene. The resulting polymer was purified by Soxhlet apparatus and dissolved hot chlorobenzene and precipitated in MeOH. The thermal analysis of the resulting polymer was evaluated by differential scanning calorimetry (DSC) measurement at the heating rate of 10°C/min. The T_g of the resulting polymer is 114 °C in second scan.

Figure 2 shows UV-Vis absorption spectrum of Poly(TT-BT) in solution and solid states. In solution, Poly(TT-BT) displayed absorbance maximum at 466 nm, which is attributed to the $\pi-\pi^*$ transition of the $\pi-$conjugated segment. In comparison with the absorption spectra in solution, the red-shifted peaks at 500 nm with shoulder at 580 nm in as-prepared film. After thermal annealing at 160°C, Absorption peak was further red-shifted. This absorption change can be resulted from aggregation and intramolecular π-π stacking of polymer chain and occurs in the solid state film [17, 18]. In voltammetric analysis, HOMO level of Poly(TT-BT) is a 5.25 eV in 0.1 M Bu_4NPF_6/acetonitrile at scan rate of 50 mV s^{-1}. Thieno[3,2-*b*]thiophene based polythiophenes [19] have relatively lower HOMO energy level than polythiophenes (P3HT and PQT-12; ca. 5.0~5.1 eV) [11–13]. The LUMO energy level is found to be 3.22 eV calculated by using the equations $E_{\mathrm{LUMO}} = E_g + E_{\mathrm{HOMO}}$. Figure 3 shows three different device configurations used in this study and Table 1 summarizes the FET characteristics of Poly(TT-BT) under ambient conditions.

To investigate the charge carrier properties of the thieno[3,2,-*b*]thiophene based polymer, top contact/bottom gate OFETs were fabricated. The Poly(TT-BT) semiconductor films were spin-coated at in air from a 1 wt% 1,2-dichlorobenzene solution heated at 60°C

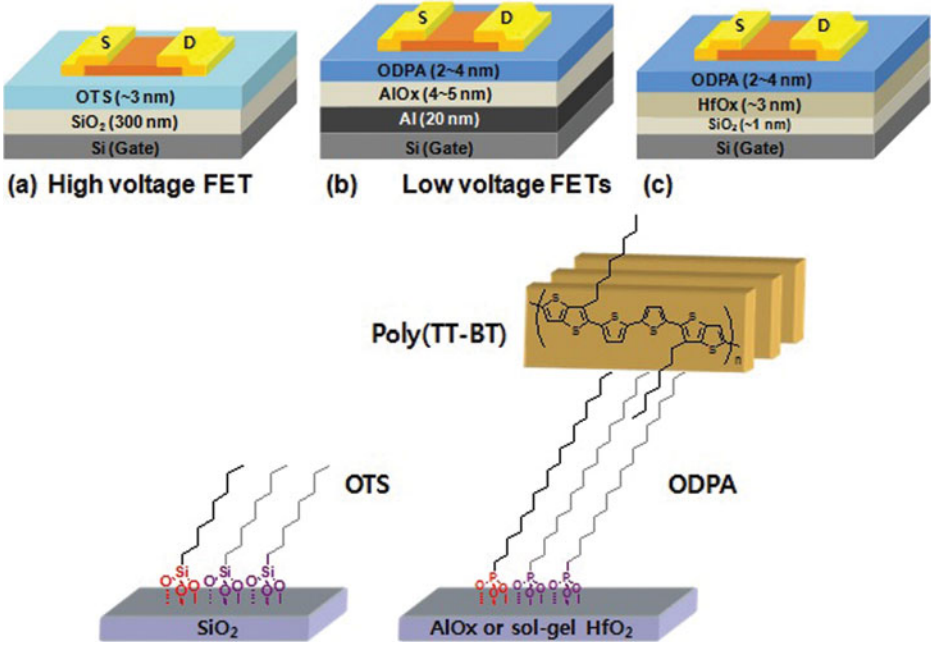

Figure 3. Three different device configurations and molecular structure used in the study.

followed by a 160°C bake on a hotplate for 10 min in an argon environment. Vacuum deposited Au was used as source and drain electrodes. Without OTS layer on SiO_2 dielectric the mobility showed 1.0×10^{-3} cm^2 V^{-1} s^{-1} with on/off current ratio of $10^3 \sim 10^4$ (Device 1). In the literature, trichloroalkyl silane moiety can be formed SAM onto inorganic gate insulators and results in enhancing the charge carrier mobility [2–4]. SAM dielectric enables us to control the charge density and increase crystallinity of the semiconducting polymer in the TFT channel [20, 21]. Applying OTS SAM on SiO_2 gate insulator, the

Table 1. Summary of device performances for Poly(TT-BT) TETs with different dielectrics ($W = 9000$ μm and $L = 90$ μm)

Device no.	Configuation	Ci (nF/cm^2)^c	μ (cm^2 /Vs)	I_{on}/I_{off}	V_t (V)	S (mV/dec)	Operating voltage
1^a	SiO_2/Si		1×10^{-3}	10^3–10^4	−10	400	
2^a	OTS/SiO_2/Si	10	4×10^{-3}	10^4	−6	200	−60 V
3^b	OTS/SiO_2/Si	10	2.3×10^{-2}	10^5–10^6	−3	200	−60 V
4^b	ODPA/AlO_x/ Al/Si	600	2.3×10^{-2}	10^4–10^5	−1.4	130	−3 V
5^a	ODPA/HfO_x/ SiO_2/Si	580	2.9×10^{-3}	10^2	−0.05	400	−1.5
6^b	ODPA/HfO_x SiO_2/Si	580	1.1×10^{-2}	10^3	−0.31	175	−1.5

^{a} as-prepared films. ^{b} annealed films at 160°C. ^{c} at 10 kHz.

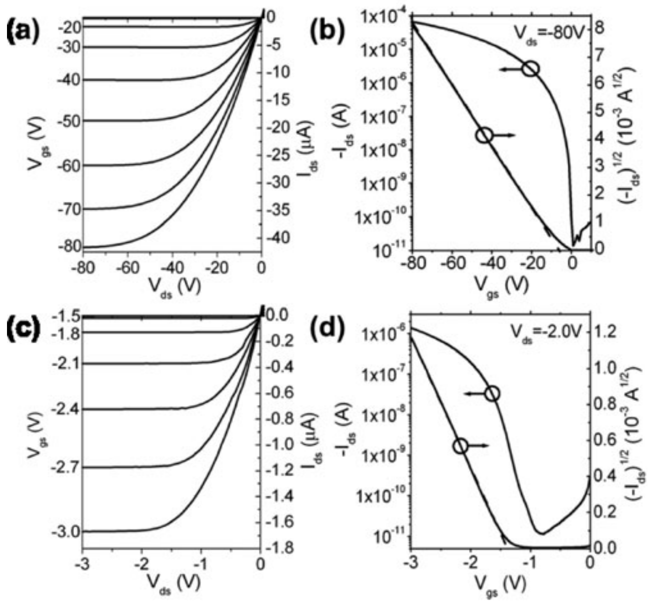

Figure 4. Current-voltage characteristics of Poly(TT-BT). (a) Output curves on OTS modified SiO_2 dielectric at different gate voltages (V_{GS}), (b) transfer curve at a constant drain-source voltage (V_{ds}) of −60 V, (c) Output curves on ODPA modified AlOx dielectric at different gate voltages (V_{GS}), and (d) transfer curve at a constant drain-source voltage (V_{ds}) of −2 V.

mobility increased four times before annealing (Device 2). Upon annealing at 160°C for 10 min, the average *p*-type mobility in the saturation regime (Fig. 4, Device 3) significantly increased to about 2.3×10^{-2} cm^2 V^{-1} s^{-1} based on more than 10 devices tested in ambient conditions with good reproducibility. This result suggests that the strong intermolecular interactions exist, which can be accounted for the $\pi-\pi$ stacking of highly π-extended polymer backbone. The device 3 showed high on/off current ratio of over 10^6, a small threshold voltage (V_t) of −3 V and a low subthreshold slope (*S*) of ca. 200 mV $decade^{-1}$ and −60 V operating voltage (Figs. 4(a) and 4(b)).

In order to decrease operating voltage of devices, high-*k* FET devices were also fabricated. The threshold voltage is inversely proportional of the capacitance of the used gate dielectric. Therefore, introduction of high-*k* dielectric of solution-processable transistor can be significantly reduced the threshold voltage. Moreover, phosphoric acid SAM can reduce the remained free-OH group due to the elimination of homo-crosslinking [2–4, 6] compared to siloxane SAM (trialkoxysilane) and selectively reacted with metal oxide [22, 23]. For these reasons, ODPA-treated aluminum oxide and hafnium oxide were used as hybrid gate dielectrics to reduce operating voltage and enhance the charge carrier mobility. To prepare ODPA-treated FET devices, a heavily n-doped silicon wafer was used as the substrate and gate electrode. Static water contact angles are <10° for plasma-treated AlOx dielectric ($C_i = 0.95$ $\mu F/cm^2$) and bare HfO_2 dielectric ($C_i = 1.04$ $\mu F/cm^2$) prepared by sol-gel process. After treatment of ODPA SAM on AlOx and HfO_2, contact angles are 105 ± 2^o of AlOx gate insulator and 110 ± 2^o of HfO_2 gate insulator. These hydrophobic nature are in accordance with literatures [7, 8, 24]. OPDA-treated AlOx transistor has the *p*-type mobility of 2.3×10^{-2} cm^2 V^{-1} s^{-1}, V_t of −1.4 V, an on/off current ratio of 10^4–10^5,

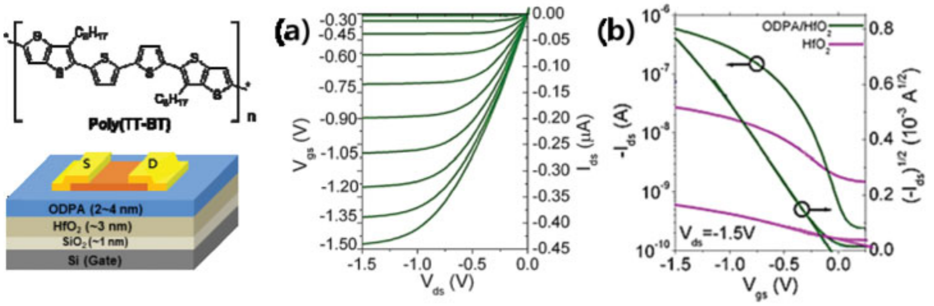

Figure 5. Current-voltage characteristics of Poly(TT-BT). (a) Output curve on ODPA modified HfO_2 dielectric at different gate voltages (V_{GS}) and (b) transfer curve at a constant drain-source voltage (V_{ds}) of −1.5 V.

and S of 130 mV decade^{-1} (Fig. 4c, d, and Device 4). These resulted in high capacitance of 0.6 μF/cm^2, which leads to decrease the threshold voltage of hybrid transistor as low as −1.4 V compared to that of a SiO_2 based transistor (Fig. 4a, 4b, and Device 3). Furthermore, lowest-voltage organic transistor is the use of HfO_2 gate dielectric based on OPDA-based self-assembled monolayers (SAMs). Figure 5 shows the typical transfer and output curves of HfO_2 hybrid dielectric for Poly(TT-BT) TFTs annealed at 160°C for 10 min. This device provides a capacitance approaching 0.58 μF/cm^2, which is higher than ODA-treated HfO_2 prepared by atomic layer deposition (0.25∼0.4 μF/cm^2 at 1 kHz) [25, 26], and thus allow organic transistors to operate with voltages of a few volts (Device 5 and 6). Before annealing, charge carrier mobility of as-prepared Poly(TT-BT) film exhibits 2.9×10^{-3} cm^2 V^{-1} s^{-1} and on/off ratio of 10^2 (Device 5). Upon annealing at 160°C, μ of 1.1×10^{-2} cm^2 V^{-1} s^{-1}, V_t of −0.31 V, I_{on}/I_{off} of 10^3, and S of 175 mV/dec at V_{ds} of −1.5 V were achieved (Device 6).

Conclusions

We have demonstrated that solution-processable 3-octylthieno[3,2-*b*]thiophene based conducting polymer, Poly(TT-BT), exhibits high charge carrier mobility with low voltage FET performances. OTS-treated SiO_2 dielectric has a field effect mobility of 2.3×10^{-2} cm^2 V^{-1} s^{-1}, on/off current ratio of over 10^6, a low threshold voltage of −3 V and V_{ds} of −60 V. The high charge carrier mobility and low operating voltage device using OPDA-anchored high-k AlOx as a gate dielectric is 2.3×10^{-2} cm^2 V^{-1} s^{-1} in the saturation region with V_{ds} of −2 V. In ODPA-treated HfO_2 hybrid dielectric, the saturated mobility is 1.1×10^{-2} cm^2 V^{-1} s^{-1} and the V_t was measured to be −0.31 V at V_{ds} −1.5 V, which is at least one order lower than SiO_2 hybrid dielectric (−3 V).

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